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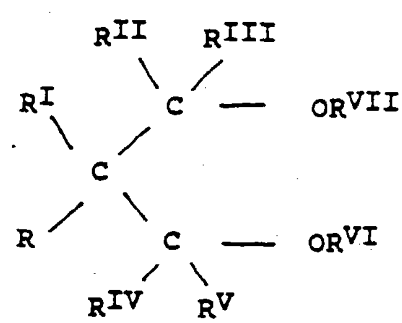
(54) Diethers usable in the preparation of Ziegler-Natta catalysts.

(57) Diethers of general formula:



where R, R^I, R^{II}, R^{III}, R^{IV} and R^V, same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R^I are not both H or CH_3 or are not CH_3 and n-propyl; R^{VI} and R^{VII} the same or different, are linear or branched alkyl, cycloaliphatic, aryl, or arylalkyl radicals having 1-18 carbon atoms; one or more of R to R^{VII} may be bonded to form a cyclic structure.

The diethers are particularly useful in the preparation of Ziegler-Natta catalysts.

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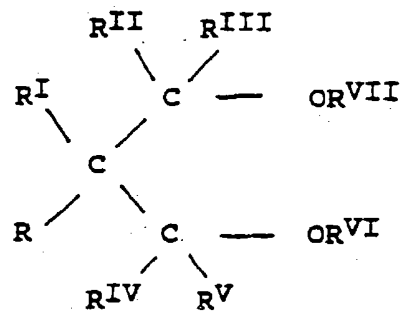
DIETHERS USABLE IN THE PREPARATION OF ZIEGLER-NATTA CATALYSTS

The present invention refers to a new class of diethers.

The diethers of the invention are useful as additives for fuels (where th y produce an increase in the octane number), as solvents, as a complexing agent for metal ions, and in the preparation of Ziegler-Natta catalysts.

The diethers have the general formula:

(I)

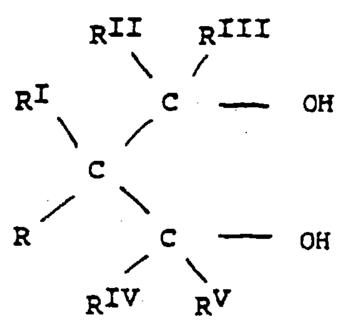


where R, R^{I}, R^{II}, R^{III}, R^{IV} and R^{V}, same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R^{I} are not both H or CH_3 or are not CH_3 and n-propyl; R^{VI} and R^{VII}, the same or different, are linear or branched alkyl, cycloalkyl, aryl, alkylaryl radicals with 1-18 carbon atoms; one or more of R to R^{VII} can be bonded to form a cyclic structure.

Preferabiy R^{VI} and R^{VII} are alkyl radicals with 1-6 carbon atoms, R^{II}, R^{III} and R^{V} are hydrogen. When R and R^{I} are alkyl radicals, they have preferabiy 3 or more carbon atoms.

The new diethers may be prepared according to various methods. For example, they may be prepared according to known etherification reactions such as the ones listed below, starting from the corresponding diols of general formula (II)

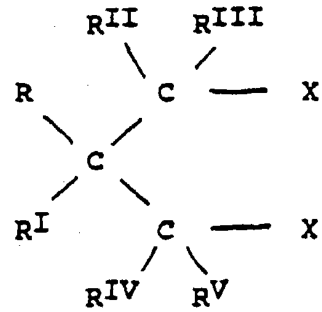
(II)



1) Reaction of diols of formula II or the corresponding alkaline alcoholates with compounds of formula R^{VI}-X, R^{VII}-X or their mixtures (where X = Cl, Br, I, C_6H_5-SO_3, p.$CH_3C_6H_5SO_3$, CH_3SO_3), wherein R, R^{I}, R^{II}, R^{III}, R^{IV} and R^{V} have the same meaning as set forth above.

2) Reaction of diols of formula II with dialkyl sulfates of formula $R_2{}^{VI}$ SO_4 or $R_2{}^{VII}$ SO_4 in alkaline environment.

3) Reaction of derivatives of general formula III, using known techniques, starting from the diols of formula II

(III) 

(wherein R to R^{V} and X have the meaning as indicated above) with R^{VI}-OM and R^{VII} OM alcoholates, wherein M = Na, K, Mg, Ca or mixtures thereof.

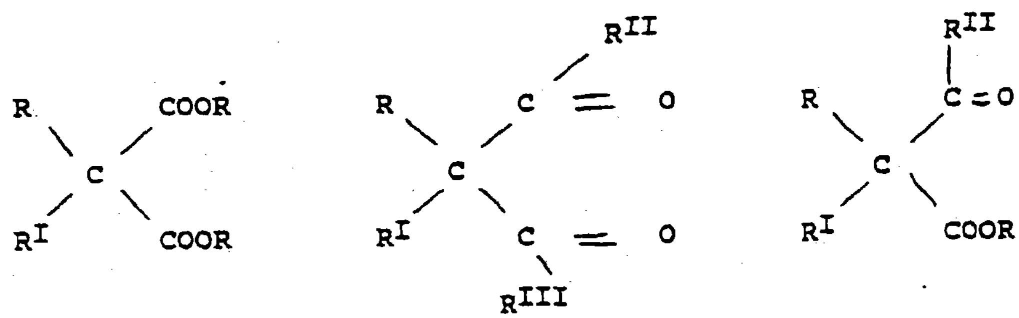
4) Thermal or catalytic dehydration of mixtures of diols of general formula (II) with R^{VI} OH or R^{VII} OH alcohols or mixtures thereof. These and other suitable methodologies are described in:

1) Houben Weil - Metoden der Organischen Chemie Vol VI/$_3$ Verlag ed. Stuttgard 1965.

2) G.W.Gokel and Coll. Syntesis 1976, 168.

3) G. Johns and Coll. ibid. 1976, 515.

4) D. Achet and Coll. ibid. 1986, 642. The diols of general formula (II) may in turn be synthetized, for example, according to known methods such as the reduction of the corresponding diesters, dialdehydes, diketones, ketoaldehydes or dicarboxylic acids, having the general formula IV and V, and ketoesters and aldehyde esters of general formula (VI)



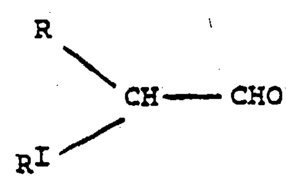
(IV) (V) (VI)

(where the radicals R, R^{I}, R^{II}, R^{III} have the meaning as indicated above).

Examples of these methods are described in:

- H. Adkins, Organic Reactions 8, 1 (1954)
- N.G. Gaylord, Reduction with Complex Metal Hydrides, Interscience Publishers, N.Y., London 1956.
- R. F. Nystrom, W. G. Brown, J. Am. Chem. Soc. 69, 1197 (1947).

Furthermore diols of formula II (wherein R^{II}, R^{III}, R^{IV}, and R^{V} are H) may also be prepared from aldehydes of general formula VII

(VII) 

wherein R and R′ have the same meaning as already specified, by action of alkaline formaldehyde

according to the Cannizzaro reaction (se for example Organic Reactions Vol II, pag. 94 -J. While ed. - N.Y., 1944).

Diols of general formula II may easily be converted into the corresponding III derivates by known methods (see Houben Weil, Methoden der organischen Chemie, Band V/3, V/4, IX; Verlag ed. Stuttgard).

The following examples illustrate the following ethers of the invention and methods of preparing same:

- 2-methyl,2-isopropyl-1,3-dimethoxypropane
- 2,2-diisobutyl-1,3-dimethoxypropane
- 2,2-diphenyl-1,3-dimethoxypropane
- 2,2-dibenzyl-1,3-dimethoxypropane
- 2,2-bis(cyclohexylmethyl)1,3-dimethoxypropane
- 2,2-diisobutyl-1,3-dibutoxypropane
- 2,2-diisobutyl-1,3-ethoxypropane
- 2-isopentyl,2-isopropyl-1,3-dimethoxypropane
- 2,2,4-ttimethyl-1,3-dimethoxypentane
- 1,1′-bismethoxymethylcyclohexane
- (+/-) 2,2′-bis(methoxymethyl)norbornane (racemic mixture).

Other examples of ethers are:

- 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane
- 2,2-diisopropyl-1,3-dimethoxypropane
- 2-isopropyl2-cyclohexylmethyl-1,3-dimethoxypropane
- 2,2-diisopentyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane
- 2,2-dicyclopentyl-1,3-dimethoxypropane
- 2-heptyl-2-pentyl-1,3-dimethoxypropane
- 2,2-dicyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-isobutyl-1,3-dimethoxypropane
- 2,2-dipropyl-1,3-dimethoxypropane.

Example 1

Preparation of 2,2-diisobutyl-1,3-dimethoxypropane.

a) Preparation of diisobutyl ethyl malonate.

Into a 250 ml flask, equipped with an agitator, refrigerant, charge funnel, thermometer and tube for the introduction of gases, were charged, under nitrogen flow, 100 g anhydrous ethanol and 5 g (0.22 moles) Na. When the dissolution of Na was complete, 16 g (0.1 moles) diethylmalonate was introduced, and stirred at room temperature for a few minutes. Then 28 g isobutyl bromide (0.21 moles) was added and the mixture was refluxed with agitation for 6 hours. Subsequently, 7.5 g dry sodium ethylate (0.12 moles) and 14 g isobutyl bromide (0.1 moles) were added. The agitation and the reflux heating was continued for 8 more hours.

Most of the solvent was distilled off at reduced pressure (50 mm Hg), and the remainder was extracted with 200 ml hexane. The distilled hexane solution provided 15.5 g of diisobutyl ethylmalonate with a boiling point of 145-146 °C/20 mm Hg. The product has a gas-chromatographic purity (main peak area) of 97.5%, and coincides with a sample of diisobutyl ethylmalonate prepared according to Bently and Perkin, J. Chem. Soc. 73, 61.

b) **Preparation of 2,2-diisobutyl-1,3-propandiol.**

Into the same apparatus as described above in a) were introduced, under nitrogen flow, 100 ml diethyl ether and 3 g $LiAlH_4$ (0.079 moles).

Then dropwise over a period of one hour while maintaining vigorous agitation, 15.5 g diisobutyl ethyl malonate from a) above was added and the mixture refluxed for 30 minutes.

The reaction mixture was then poured into a vessel containing 100 g ice acidified with dil. HCl and extracted with 3 portion of 100 ml of ethyl ether.

The ether was evaporated and 10 g of a raw material was produced which, when crystallized from hexane, gave 8.5 g of 2,2-diisobutyl-1,3-propandiol with melting point 75-77 °C and an elemental analysis of C = 70.3% and H = 12.6%. The theoretical value for $C_{11}H_{24}O_2$ is C = 70.21% H = 12.7%.

c) **Preparation of 2,2-diisobutyl-1,3-dimethoxypropane.**

Into the same apparatus as described above in a) was introduced, under nitrogen, 8.5 g (0.06 moles) 2,2-diisobutyl-1,3-propandiol, 200 ml dioxane and 15.4 g (0.136 moles) potassium tert-butylate.

The mixture was stirred at room temperature for 30 minutes and then 20 g CH_3I (0.14 moles) was added dropwise. During this procedure, the temeperature rises spontaneously to 50 °C.

After 2 hours, an additional quantity of potassium tert-butylate (154 g, 0.136 moles) and of CH_3I (20 g, 0.14 moles) was added, and the mixture refluxed for 1 hour. The reaction mass was filtered and the filtrate distilled at reduced pressure. Among other products, 7.4 g of 2,2-diisobutyl-1,3-dimethoxypropane having a boiling point 100-101 °C/22 mm-Hg which by gas layer cromatography (GLC) shows a purity of 99% (chromatographic peaks area) was obtained.

$n^D{}_{20}$ = 1.4337.

^{1}HNMR (300 MHz, $CDCl_3$, TMS as internal standard):

signals at 0.89 ppm, doublet 12 H

1.21 ppm, doublet 4 H

1.68 ppm, multiplet 2 H

3.16 ppm, singlet 4 H

3.26 ppm. singlet 6 H

Using the procedures of a), b) and c) above the following compounds were obtained:

1) 2-methyl-2-isopropyl-1,3-dimethoxypropane $n^D{}_{20}$ = 1.4209, boiling point 160 °C-161 °C/$_{760\ mmHg}$
2) 2,2-dibenzyl-1,3-dimethoxypropane p.f. 105 °C (from petroleum ether)
3) 2,2-diisobutyl-1,3-dibutoxypropane $n^D{}_{20}$ = 1.4378, boiling point 115 °C-117 °C/$_{1\ mmHg}$
4) 2,2-diisobutyl-1,3-diethoxypropane $n^D{}_{20}$ = 1.4302, boiling point 118 °C-120 °C/$_{20\ mmHg}$

Example 2

Preparation of 2,2-bis(cyclohexylmethyl)-1,3 dimethoxypropane.

Into a stainless steel autoclave provided with an anchor agitation system, 5.8 g (0.02 moles) of $(C_6H_5CH_2)_2C(CH_2OCH_3)_2$ prepared according to example 1, 100 ml n-hexane and 10 g Raney Ni washed by decanting with 3 parts 50 cc anhydrous ethanol and subsequently with 3 parts 50 cc of hexane, were introduced.

The autoclave was pressurized with 17 atm. of hydrogen and was heated to 135 °C (internal temperature) for 8 hours with agitation.

After cooling, the reaction mixture, was filtered from the catalyst and vacuum evaporated, to yield 5.9 g of a colorless oil with a purity of 99% $n^D{}_{20}$ = 1.4790. The only compound detectable by thin layer chromatography (TLC), was 2,2-bis(cyclohexyl,methyl)-1,3-dimethoxypropane.

^{1}HNMF(300 MHz, $CDCl_3$, TMS as internal standard).

Signals at:

0.96 ppm multiplet 4 H

1.18 ppm multiplet 12 H

1.63 ppm multiplet 10 H

3.15 ppm singlet 4 H

3.27 ppm singlet 6 H

Example 3

Preparation of 2,2-diphenyl-1,3-dimethoxypropane.

a) Preparation of 2,2-diphenyl-1,3-propandiol.

Into the same apparatus described in example 1 (a)), 10.6 g (0.054 moles) of $(C_6H_5)_2CHCHO$ (Fluka), 4.03 g (0.028 moles) K_2CO_3, 10 cc water, 13.2 ml acqueous formaldehyde at 40% (0.176 moles) and 35 ml ethanol at 99% purity were introduced.

The mixture was stirred and refluxed for 6 hours, cooled and diluted with 200 ml of water. The precipitate thus formed was filtered, washed with water and crystallized from benzene to give 9.6 g of 2,2-diphenyl-1,3-propandiol with a m.p. 102-104 °C.

b) **Preparation of 2,2-diphenyl-1,3-dimethoxypropane.**

Into the same apparatus as described in a) was charged 9.6 g 2,2-diphenyl-1,3-propandiol dissolved in 400 ml anhydrous tetrahydrofuran and stirred under nitrogen with 3.8 g NaH (55% NaH dispersed in vaseline oil) until the production of hydrogen stops. Over a period of 20 minutes, 9.6 ml CH_3I was added and stirring continuously for 2 hours. Most of THF was distilled off; then the product is diluted with water (200 ml) and extracted with two 50 ml portions of diethyl ether. The ether extract gives, by vacuum distillation, 3.5 g of 2,2-diphenyl-1,3-dimethoxypropane having boiling point of 188 °C-190 °C/$_{20\ mm\ Hg}$ which was unitary by TLC-chromatography and having
n^{D}_{20} = 1.5558.

According to the same procedure described above in a) and b) the following compounds were prepared starting respectively from hexahydrobenzenaldehyde and norbornan-2-carboxhaldehyde.

A) 1,1-dismethoxymethylcyclohexane boiling point 97 °-98 °C/$_{20\ mm\ Hg}$; n^{D}_{20} = 1.4487 ^{1}HNMR (300 MHz, $CDCl_3$, TMS as internal standard): signals at:
1.36 ppm multiplet 10 H
3.20 ppm singlet 4 H
3.29 ppm singlet 6 H

B) (+/-) 2,2-dismethoxymethylnorbornane boiling point 106 °-108 °C/$_{20\ mm\ Hg}$; n^{D}_{20} = 1.4659 ^{1}HNMR (300 MHz, $CDCl_3$, TMS as internal standard) Signals at:
0.72 ppm doublet 1 H
1.14 ppm doublet 1 H
1.06 ppm multiplet 1 H
1.34 ppm multiplet 2 H
1.51 ppm multiplet 3 H
1.97 ppm singlet (broad) 1 H
2.15 ppm singlet (broad) 1 H
3.06 ppm system AB 1 H
3.14 ppm system AB 1 H
3.33 ppm system AB 1 H
3.36 ppm system AB 1 H
3.29 ppm multiplet 6 H

Example 4

Preparation of 2,2,4-trimethyl-1,3-dimethoxypentane.

Into a 2 l flask provided with an agitator, refrigerant, charge funnel, thermometer and tube for the introduction of gases, are charged, under nitrogen flow:
29.2 g (0.2 moles) 2,2,4-trimethyl-1,3-propandiol, 600 ml dioxane, and 10 g (0.2 moles) NaH at 50% concentration in vaseline oil. The contents were agitated until the production of gas ceased; then heated to 80 °C, and 18 ml CH_3I (0.28 moles) was introduced dropwise. After two hours 10 g NaH at 50% concentration (0.2 moles) in vaseline oil and 40 cc CH_3I (0.62 moles) were added.

After reflux heating for 8 hours the reaction mixture was diluted with 1.5 l of water and extracted with 3 portions of hexane (100 ml each).

Th xtract was washed with water and dried, and on vacuum distillation, gave 22.5 g of 2,2,4-trimethyl-1,3-dimethoxypropane having a boiling point 105° C/70 mm Hg whose purity (peak areas) is 98.6% by GLC and

n^{D}_{20} = 1.4227

^{1}HNMR (60 MHz, $CDCl_3$, TMS as internal standard)

signals at:

1.5 ppm multiplet 12 H

3.7 ppm multiplet 3 H

4.1 ppm multiplet 6 H

Example 5

Preparation of 2-isopentyl-2-isopropyl-1,3-dimethoxypropane.

a) **Isopentylidenisopentanale preparation.**

50 g isopentanale are reacted according to the procedures described in DRP 643341 (1933 I.G. Farb.) and DRP 544192 (1933 I.G. Farb.).

27 g of 2-isopentyldeneisopentanale, having a boiling point 98-102° $C/_{20\ mm\ Hg}$ are obtained.

b) **Preparation of 2-isopentylisopentanale.**

Following the hydrogenation method described by J. V. Braun and G. Manz, Ber. 1969, 67 (1934) starting from 27 g 2-isopentyldeneisopentanale, 27 g of raw material was obtained which was not characterized. The hydrogen absorption measured was consistent with the reaction reported.

c) **Preparation of 2-isopropyl-2-isopentyl-1,3-propandiol.**

Into the same apparatus of example 1 a) 27 g raw aldehyde from the preceding preparation for b), 16 g K_2CO_3, 200 ml 99% pure ethanol and 52 ml aqueous CH_2O at 40% concentration were introduced, and maintained at reflux with agitation for 4 hours. Then the reaction mixture was diluted with 1 l water, extracted with two 250 ml portions of ether. The ether was evaporated and the ether extract dried and distilled at reduced pressure providing (among other compounds) 9 g of 2-isopropyl-2-isopentyl-1,3-propandiol having a boiling point of 165° C/20 mm Hg and being unitary by TLC. This material was used for the next reaction without further analysis.

d) **Preparation of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane.**

Into the apparatus of example 1 a) under nitrogen flow, 9 g of raw material from c) above, 200 cc dioxane, and 15 g $(CH_3)_3COK$ (potassium terbutylate) were charged and agitated for about 30 minutes. Then 10 ml CH_3I was introduced over a period of one hour, and the contents refluxed for 5 hours. The reaction mixture was diluted with 1 l water and extracted with diethyl ether. The ether was evaporated and the ether extract dried and distilled at reduced pressure. Among other compounds, 7.3 g of 2-isopropyl-2-isopentyl-1,3-dimethoxypropane having a boiling point of 130-133° C/35 $_{mm}$ H_g and a gas-chromatographic purity of 98.6% (peak areas).

n^{D}_{20} = 1.4365

^{1}HNMR (300 MHZ, $CDCl_3$, TMS as internal standard) signals at:

0.87 ppm douplet 6 H

8.89 ppm douplet 6 H

1.11 ppm multiplet 2 H

1.28 ppm multiplet 2 H
1.42 ppm multiplet 1 H
1.76 ppm multiplet 1 H
3.23 ppm singlet 2 H
3.24 ppm singlet 2 H

Example 6

In a 500 ml flask was introduced, under agitation, 60 ml n-heptane and 67 ml tetra-n-butoxy-titanium, and heated to 45° C. Over a period of three hours, a solution of Al Et_2Cl (44.8 ml) in n-heptane (108 ml) was gradually introduced.

The temperature was raised to 60° C for one hour and then cooled to room temperature.

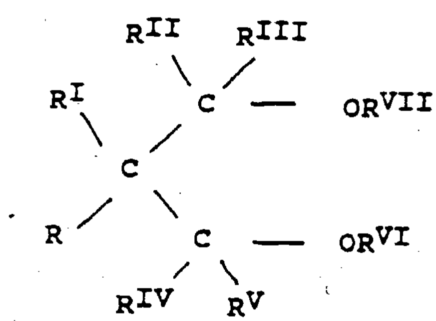
A solid was separated and washed four times with 100 ml portions heptane and then vacuum dried.

Into a flask, 8.1 g of this solid was introduced together with 20.3 m moles titanium tetrachloride, 20.3 ml toluene, and 20.3 m moles 2,2-diisobutyl-1,3-dimethoxypropane and heated to 60° C for one hour, and then at 100° C for 4 hours. The reaction mixture was then cooled at room temperature, the solid product was separated,washed with n-heptane until no chlorine ions were in the filtrate and dried in an oven under nitrogen flow.

In a 120 ml autoclave equipped with a magnetic agitator are introduced, after drying under nitrogen flow, 250 mg Al Et_2Cl, 12.4 mg of the solid prepared above, and 80 ml liquid propylene, and heated to 60° C and maintained at this temperature for one hour under agitation. The excess unreacted propylene was discharged and 16.9 g of polypropylene was obtained with an isotactic index of 96.8% (extraction with n-heptane boiling for 4 hours).

Claims

1. Diethers of formula:



where R and R^I, R^{II}, R^{III}, R^{IV} and R^V same or different, are H or linear or branched alkyl, cycloalkyl, aryl, alkyaryl or arylalkyl radicals with 1-18 carbon atoms, provided that R and R^I are not both H or CH_3 or are not CH_3 and n-propyl; R^{VI} and R^{VII} are the same or different and are linear or branched alkyl, cyclcoalkyl, aryl, alkylaryl radicals with 1-18 carbon atoms; one or more of R to R^{VII} can be bonded to form a cyclic structure.

2. Diethers according to claim 1 wherein R^{VI} and R^{VII} are alkyl radicals with 1-6 carbon atoms, R^{II}, R^{III}, R^{IV} and R^V are hydrogen, and when R and R' are alkyl radicals, they have 3 or more carbon atoms.

3. Diethers according to claim 2 selected from the group consisting of:

- 2,2-diisobutyl-1,3-dimethoxypropane
- 2,2-diphenyl-1,3-dimethoxypropane
- 2,2-dibenzyl-1,3-dimethoxypropane
- 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane
- 2-isopentyl-2-isopropyl-1,3-dimethoxypropane
- 2-isopropyl-2-3,7-dimethyloctyl-1,3-dimethoxypropane
- 2,2-diisopropyl-1,3-dimethoxypropane

- 2-isopropyl-2-cyclohexylmethyl-1,3-dimethoxypropane
- 2,2-diisopentyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane
- 2,2-dicyclopentyl-1,3-dimethoxypropane
- 2-heptyl-2-pentyl-1,3-dimethoxypropane
- 2,2-dicyclohexyl-1,3-dimethoxypropane
- 2-isopropyl-2-isobutyl-1,3-dimethoxypropane
- 2,2-dipropyl-1,3-dimethoxypropane

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 89118025.9

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	CHEMICAL ABSTRACTS, vol. 99, no. 5, Columbus, Ohio, USA WHALON, MICHAEL R. et al. "A remarkable consistency in conformational preference for a series of 1,3-disubstituted-2,2-dimethylpropanes" page 478, column 1, Abstract-no. 37 911t & Tetrahedron Lett. 1982, 23(50), 5247-50	1	C 07 C 43/10
A	DE - C - 888 999 (CHEMISCHE WERKE HÜLS) * Example; claim *	1	
A	US - A - 3 290 387 (CLAUDE BERNARDY et al.) * Column 1, lines 16-33; claim 1 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A,E	CHEMICAL ABSTRACTS, vol. 84, no. 24, Columbus, Ohio, USA MC ALEES, ALAN J. et al. "Complexes of titanium tetrachloride with terdentate triped ligands. Competition among oxygen, sulfur and nitrogen for coordination sites on titanium" page 593, column 1, Abstract-no. 173 108d & Inorgan. Chem. 1976, 15(5), 1065-74	1	C 07 C 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	02-01-1990	REIF

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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P : intermediate document

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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document